

## Role of Hydrogen in C and Si (001) Homoepitaxy

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We present *ab initio* studies of adsorption of half a monolayer of carbon atoms on a C(001)-(2 × 1):H surface and of silicon atoms on a Si(001)-(2 × 1):H surface. We find that the hydrogen atoms migrate spontaneously on C(001), while they remain stuck at their initial configuration on Si(001). These results are consistent with the experimental facts on hydrogen mediated epitaxies of diamond and silicon: The presence of hydrogen is helpful to diamond epitaxy and intrusive to silicon epitaxy. We propose that atomic hydrogen acts as a surfactant on C(001) homoepitaxy.

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Considerable interest [1–3] has been focused on the growth technique of epitaxial semiconductor films by assistance of atomic hydrogen because of its practical efficiency. Success of diamond synthesis under atmospheric pressure and temperature by the chemical vapor deposition (CVD) method is a most dramatic example [4,5].

From a fundamental point of view, we can see interesting and contrasting facts in hydrogen mediated epitaxies of fourth row semiconductors. In the case of silicon epitaxy, using atomic hydrogen is known to be disruptive for the homoepitaxy on Si(001) so that hydrogen must be removed from the surface to grow a silicon crystal [2]. On the other hand, quite a high concentration (over 90%) of hydrogen gas is required to grow a CVD diamond [6].

Why are hydrogen atoms on the diamond surface not disruptive to the growth of the diamond crystal? We believe that there is an essential difference in the electronic structures of hydrogenated C(001)-(2 × 1) and Si(001)-(2 × 1), which can be seen, for example, from the electronegativity of hydrogen, which is in between that of carbon and silicon, i.e.,  $e_C > e_H > e_{Si}$  (2.5, 2.2, 1.8, respectively, by Pauling's definition).

To clarify these differences from the microscopic point of view, we study the electronic structure and the optimized geometry of both hydrogenated C and Si (001)-(2 × 1) surfaces, by means of the *ab initio* total energy calculation method. We then perform adiabatic adsorption simulations of a carbon atom on C(001)-(2 × 1):H and of a silicon atom on Si(001)-(2 × 1):H. To retain the two-dimensional periodicity of the surface, we actually consider half monolayers of C or Si adsorbates.

The simulation method [7] is based on density-functional theory within the local-density approximation. The Troullier-Martins' (TM) norm-conserving nonlocal pseudopotentials were used in the separable form. The

total energies for arbitrary structures were calculated by adopting the conjugate-gradient method to a minimization of electronic degree of freedom. Since plane waves were used as a basis set, surfaces were modeled by periodic slab models. The bulk lattice constants of diamond and silicon were fixed to be 3.57 and 5.43 Å, respectively, which correspond to the experimental values. While the periodicity of the surface unit cell was taken to be 2 × 1 throughout our simulations, we used two types of periodicities for surface normal direction.

In the case of optimizing the surface geometry, the slab consisted of ten atomic layers and a vacuum region of thickness equivalent to ten atomic layers. All atoms in the slab were then relaxed, until the maximum absolute value of the force acting on each atom ( $F_{max}$ ) became less than 0.005 Ry/bohr. The cutoff energy ( $E_{cut}$ ) for the plane-wave expansion was set at 36 Ry and the primitive first Brillouin zone was sampled with four  $\mathbf{k}$  points ( $N_k = 4$ ). We confirmed that the above parameter set was suitable to get a converged geometry, by varying  $E_{cut}$  from 20 to 81 Ry,  $F_{max}$  from 0.01 to 0.001 Ry/bohr, and  $N_k$  from 1 to 8.

For simulating adsorption, the thickness of the slab and the vacuum region was reduced to six and eight atomic layers, respectively, to save computational cost. For those simulations, higher convergence was required, since a significant reconfiguration of the surface was caused by the adsorption. The carbon atoms on the first four atomic layers of the substrate and the hydrogen atoms on the surface were relaxed. The rest of the atoms, i.e., the carbon atoms on the two layers at the bottom of the slab, were fixed in their bulk positions, and the dangling bonds on the bottom of the slab were terminated by hydrogen atoms. We have checked the correctness of this treatment by comparing the optimized geometry of the bare C(001)-(2 × 1) surface

and its reconstruction energy with the more general treatment mentioned in the previous paragraph. The parameters  $E_{\text{cut}}$ ,  $F_{\text{max}}$ , and  $N_k$  were set at 45 Ry, 0.001 Ry/bohr, and 4 points, respectively. We tested the accuracy of our calculation both structurally and energetically by optimizing hydrocarbon molecules of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . The deviations of the bond lengths of the calculated values from experimental values were no more than 1.5% and 0.5% for C-H and C-C, respectively. The enthalpy of the reaction  $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$  was calculated to be 1.9 eV, including zero-point energies evaluated from the experimental data of the normal vibration frequencies. In comparison, the experimental value is 1.6 eV. We believe that this difference of 0.3 eV per reaction is sufficiently small to justify our results.

We now proceed to the results of our calculations. First, we have optimized the surface geometries of the bare and the hydrogenated  $\text{C}(001)-(2 \times 1)$  surfaces. Although there has been no confirmative experimental observation of the *bare*  $\text{C}(001)$  surface so far, it is highly plausible to postulate that the surface undergoes dimerization as a reconstruction, from the analogy with that of a  $\text{Si}(001)$  surface [8]. As for the hydrogenated  $\text{C}(001)$ , a  $2 \times 1$  LEED pattern has been observed [9]. Scanning tunneling microscopy (STM) images on monohydride  $\text{C}(001)-(2 \times 1)$  surfaces show dimer rows [10]. These results are currently assigned to a monohydride dimer structure where each dangling bond of the dimers is terminated by a hydrogen atom. The main purpose here is to clarify the different behavior of  $\text{C}(001)$  and  $\text{Si}(001)$  surfaces upon H adsorption.

On the clean  $(001)-(2 \times 1)$  surface, a symmetric dimer was found to be favored with a dimer-bond length of 1.38 Å, in good agreement with previous theoretical results [11–13]. This symmetric structure of the dimer is in contrast to that of the  $\text{Si}(001)$  surface with a  $c(4 \times 2)$  or  $p(2 \times 2)$  reconstruction composed of asymmetric dimers [8]. The dimer bond length is very close to the  $\text{C}=\text{C}$  bond length of a  $\text{C}_2\text{H}_4$  molecule, i.e., 1.34 Å. Similar contrast of surface reconstruction between diamond and silicon, i.e., strong dimerizing without buckling on diamond and weaker dimerizing with buckling on silicon, can be seen on the  $(111)-(2 \times 1)$  surfaces. The origin of these differences has been identified as a result of a competition between a  $\pi$  bond and a Jahn-Teller distortion [12–15].

For the monohydride surface, the dimer-bond length was found to be 1.62 Å, in good agreement with previous theoretical results [11,12]. This C-C bond length is considerably larger than that in a  $\text{C}_2\text{H}_6$  molecule, 1.53 Å, suggesting that the  $\pi$  and  $\sigma$  bonding of the dimer is strongly reduced by adsorption of H atoms.

The disappearance of the strong  $\pi$  and  $\sigma$  bonding can be interpreted as a consequence of the hydrogenation of the  $\text{C}(001)$  surface, which strongly relaxes the bonding character peculiar to carbon. Here, we found a clear

contrast in the charge distribution between the  $\text{C}(001)-(2 \times 1):\text{H}$  and the  $\text{Si}(001)-(2 \times 1):\text{H}$ . The charge accumulation around the carbon dimer from hydrogen atoms can be seen in Fig. 1(a), reflecting the larger electronegativity of carbon compared to hydrogen, while electrons are rather attracted around the hydrogen atoms from a silicon dimer [Fig. 1(b)], in which the bond lengths of the Si-Si dimer and the Si-H are 2.40 and 1.52 Å, respectively. These different charge distributions affect the reaction processes between diamond and silicon epitaxies.

We now discuss the results of adsorption of carbon on the hydrogen-covered diamond surface. The adsorption was simulated using the  $2 \times 1$  surface unit cell. The adsorption site was chosen to be above the dimer center since this site is the most active for the adsorption [16], and the adsorption path is along the line normal to the surface. The adiabatic potential curves were calculated by optimizing the positions of substrate surface atoms for each fixed position of the adatom along this line [see Fig. 2(a)].

Figure 2(b) shows the total energy of C on  $\text{C}(001)-(2 \times 1):\text{H}$ , as a function of  $h$ . The energies are measured relative to the total energy at the largest considered value of  $h$ . From the figure, we can observe a drastic change in the total energy. As the adatom moves closer to the surface along the line from the highest point, the energy gradually drops around  $h = 2.9$  Å and goes up about 0.7 eV until  $h = 1.8$  Å. Going past the barrier top, the total energy discontinuously drops with a large energy gain (5.5 eV), which follows a remarkable rearrangement of the surface geometry. When the adatom is inserted in the bridge position, we can see the bond exchange, i.e., the disappearance of the original dimer bond and the appearance of new bonds between the adatom and the two atoms that formed the dimer originally. At the same time, the hydrogen atoms which had stuck on the dimer atoms spontaneously move up onto the adatom, and then

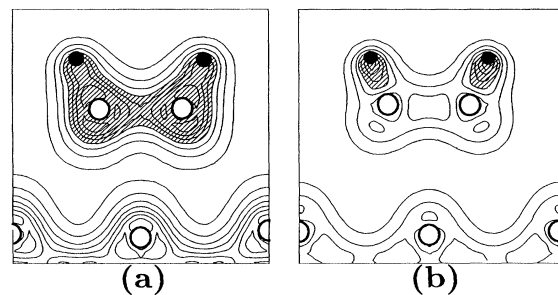


FIG. 1. Charge density plots of the monohydride  $\text{C}(001)-(2 \times 1)$  surface (a), and the monohydride  $\text{Si}(001)$  surface (b). The open circles denote C and Si atoms in (a) and (b), respectively, and the closed circles denote hydrogen atoms. The area in which the value of the charge density is over one-half of the maximum value is hatched. The lattice constants are not drawn to scale.

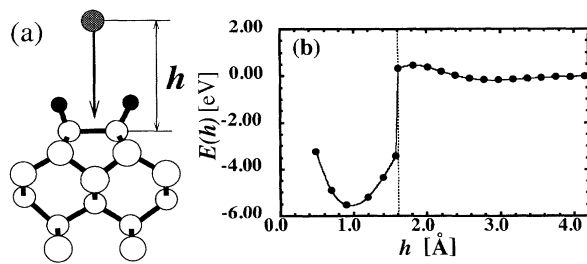


FIG. 2. (a) Schematic illustration of the monomer adsorption. Open and closed circles represent substrate and hydrogen atoms, respectively. An adatom (grey circle) is placed above the dimer center of the surface. (b) The total energy curve of C on C(001)-(2 × 1):H as a function of  $h$ . We have set  $E(h_{\max}) = 0$ . The data points correspond to the solid circles. The solid curve and the vertical dashed line are guides to the eye.

these two hydrogen atoms and the adatom form a canted dihydridelike structure [17], because we consider half monolayer adsorption [see Fig. 3(a)]. In other words, the hydrogen atoms segregate spontaneously on the growth front as a result of the adsorption. The discontinuity in the total energy curve is caused by this remarkable reconfiguration of the surface hydrogens.

The disruptive role of the atomic hydrogen on the Si(001) homoepitaxy has been found by Copel and Tromp [3] and Wolff *et al.* [2]. It is noticeable that to grow the silicon crystal hydrogen atoms have to be removed by heating the substrate [2], while on the C(001) surface mean coverage of hydrogen is extremely high under the typical CVD condition (about 98% at 1000 K) [18]. Thus we expect essential differences in the surface responses to the adsorption of carbon on C(001)-(2 × 1):H or silicon on Si(001)-(2 × 1):H. To highlight this contrast, we performed a silicon atom adsorption simulation on the monohydride (001) surface of silicon. We found that the Si-H bonds of the monohydride dimer could not be broken by the adsorption of the silicon atom. This means that hydrogen atoms hardly segregate to the growth front on the Si(001) surface,

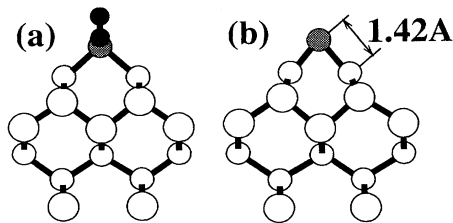


FIG. 3. (a) Optimized structure of a C atom adsorbed on C(001)-(2 × 1):H. (b) Optimized structure of a C atom adsorbed on C(001)-(2 × 1) without hydrogen atoms. The bond length of 1.42 Å between the adatom and the dimer atoms gives evidence for the  $sp^2$ -like electronic states around the original dimer atoms. Note that the  $sp^2$  bond length of graphite is 1.42 Å.

which is consistent with the experimental facts [2,3]. In the final structure, the lengths of the Si-H bond and the Si-Si bond between the adatom and the former dimer atom are 1.52 and 2.32 Å, respectively. In this study, we did not evaluate the exact energy barrier for this substitutional adsorption process, since the transition state has to be determined in the configuration space. However, we believe that the potential structures for hydrogen migration on C(001) and Si(001) surfaces are so different that on the C(001) surface hydrogen atoms can segregate below the temperature of hydrogen desorption from the surface, while on the Si(001) surface hydrogen cannot segregate below the temperature of hydrogen desorption from the surface.

Here we attempt to explain why the hydrogen atoms segregate only on C(001). We believe that the different behavior of hydrogen atoms at C(001) and Si(001) originates from the different bonding nature of carbon from silicon: carbon prefers the multiple bond much more than silicon.

When the carbon adatom is bound in the bridge configuration, both dimer atoms become threefold coordinated with the carbon atoms, i.e., the adatom and the two carbon atoms of the subsurface. In other words, the local coordination of the former dimer atom becomes that of graphite, while the coordination of the adatom is similar to the edge of the graphite sheet.

Therefore, the adatom as well as the original dimer atoms try to make  $\pi$  bonds between each other, using the two excess electrons of the adatom and the C-H bonding electrons. The electrons in the C-H bonds are attracted to the carbon adatom because of the larger electronegativity of carbon, as compared to hydrogen.

The evidence of this aptness to make  $sp^2$ -like electronic states around the original dimer atom can be seen from Fig. 3(b), which is a fully optimized carbon adsorbed C(001)-(2 × 1) surface without hydrogen atoms. A quite flat threefold coordinated geometry with 1.42 Å of interatomic distance can be seen around the original dimer atom.

As a consequence, the C-H bond is broken, and the hydrogen atoms migrate to the dangling bonds of the adatom along the  $\pi$  bonding between the adatom and the former dimer atom, being partially bound in the  $\pi$  electrons. This is the reason for the absence of energy barrier for the migration. The electronic state around the dimer is  $sp^3$  following a lone pair rather than  $sp^2$ . This can be recognized by the almost tetragonal angles between the bonds of the dimer atoms [see Fig. 3(a)]. Thus the electronic states of the surface will remain  $sp^3$  even if the origin of the migration comes from carbon's aptness to make an  $sp^2$  bond.

The above conjecture is consistent with Ref. [19]. The  $\pi$  bond is passive in reacting with hydrogen atoms, and the edge of the graphite sheet actively reacts with the atomic hydrogen.

The canting of the dihydride structure is known to be an artifact caused by a small unit cell [17]. Therefore, to avoid this artificial canting one should use a larger unit cell and perform the simulations by varying the coverage from its smallest limit to 1. Although we could not perform such realistic simulations because of computational limitations, we conjecture the results.

In the lower coverage limit, an isolated dihydride structure without canting will be the resulting structure of an adsorption, since there is no steric repulsion between the dihydrides in adjacent unit cells. In the higher coverage case, more than two dihydrides must adjoin somewhere. For simplicity, we consider only the case where two dihydrides are adjoining. In this case, the dihydrides repel each other by the steric repulsion. Because of the distortion, these dihydrides should be fragile and can be broken easily by thermal fluctuations or by the collisions with molecules (atoms) from the vapor phase. Therefore, two of four hydrogen atoms on these dihydrides will make a hydrogen molecule and evaporate. A monohydride dimer *as a new monolayer* will then appear. To examine how probable this process is we calculate the total energies of the following two structures: (1) two canted dihydrides in a  $2 \times 1$  unit cell and (2) one monohydride and one hydrogen molecule in the same unit cell. The latter case has an energy  $1.57 \text{ eV}/2 \times 1$  cell lower than the former case, which is consistent with the above conjecture.

In summary, we have performed *ab initio* adsorption simulations of C/C(001)-(2  $\times$  1):H and Si/Si(001)-(2  $\times$  1):H. We found that hydrogen atoms segregate without a substantial energy barrier only in the case of C/C(001)-(2  $\times$  1):H. We propose that diamonds will grow layer by layer by following the segregation of hydrogen on the C(001) homoepitaxy. Apart from eliminating the graphitic fragments [4], hydrogen will act *as a surfactant* [20,21] to the C(001) homoepitaxy.

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